Carbonate production by calcareous red algae and global change

Daniela BASSO
University of Milano-Bicocca,
Department of Geological Sciences and Geotechnologies,
Piazza della Scienze 4, I-20126 Milano (Italy)
daniela.basso@unimib.it

ABSTRACT
The most important groups of modern red calcareous algae are the Mg-calcite secreting Corallinales and Sporolithales, and the aragonitic Peyssonneliales and Nemaliales. They are common on the world’s shelves and are vulnerable to the global warming and the lowering of pH of sea water, caused by the ongoing increase in anthropogenic CO₂. Among them, coralline algae are ecosystem engineers and major producers of carbonate sediment, of particular importance in temperate and cold seas. Corallines respond to marine acidification and rising temperature showing decreased net calcification, decreased growth and reproduction, as well as reduced abundance and diversity, leading to death and ecological shift to dominant non-calcifying algae. Despite their key ecological and sedimentological role, and because of their vulnerability to marine warming and acidification, our knowledge of the distribution of coralline-dominated habitats and the quantification of their carbonate production is not adequate to allow proper environmental management and confident modelling of a global carbon budget. Locating the algal carbonate factories around the world, then describing them, e.g., evaluating their extent and their production, are a priority for future research.

KEY WORDS
marine acidification, carbonate sediment, carbonate production, Rhodophyta, coralline algae, habitat mapping.

RÉSUMÉ
Production carbonatée par les algues rouges calcaires et changement climatique global. Les groupes les plus importants d’algues rouges calcaires actuelles sont, d’une part, les Corallinales et les Sporolithales, qui sécrètent de la calcite magnésienne, et d’autre part, les Peyssonneliales et les Némaliales, qui produisent de l’aragonite. Abondantes sur les plates-formes actuelles, elles y jouent un rôle majeur...
INTRODUCTION

The industrial revolution of the mid-18th century was driven by a rising exploitation of fossil fuels and produced an increasing atmospheric partial pressure of carbon dioxide ($pCO_2$) from a pre-industrial level of 280 to 370 ppm in 2000. A concentration of about 560 ppm, double the pre-industrial level, is expected by 2070 (Meehl et al. 2007).

Model predictions for atmospheric $[CO_2]$ between AD 2100 and 2300 provide a wide range of values (450-8110 ppm; Caldeira & Wickett 2005), depending on variable assumptions and uncertainties about the future emission pathways (Sundquist 1993; Wigley et al. 1996; Caldeira & Wickett 2005). Among the possible scenarios, an intermediate $[CO_2]$ ranging from 1500 to 2100 ppm would be comparable to the Eocene atmosphere (Pearson et al. 2009). During the past 24 million years, atmospheric $[CO_2]$ has remained more or less stable, below 500 ppm (Pearson & Palmer 2000; Lüthi et al. 2008), with the glacial-interglacial fluctuations over the past 800 kyr corresponding to a 172-300 ppm oscillation of atmospheric $[CO_2]$ (Lüthi et al. 2008; Hönisch et al. 2009).

Atmospheric carbon dioxide is a greenhouse gas, which is warming the atmosphere and the surface ocean. Models estimate a mean global temperature in the late 21st century of about 2 to 3°C above pre-industrial temperatures. The mid-Pliocene is the most recent interval of geological time when the Earth experienced such temperature (Haywood et al. 2000; Jansen et al. 2007), although it seems that the current climate change will be much more rapid, thus decreasing the possibility of the biota’s adaptation to the new conditions.

About half of the anthropogenic CO$_2$ emission remains in the atmosphere and contribute to the enhancement of the greenhouse effect and climate change. The increase in atmospheric $[CO_2]$ is accompanied by increased gas transfer into the ocean surface waters (Houghton et al. 1992; Keeling & Whorf 1994; Takahashi et al. 1997). Since the beginning of the industrial era, the ocean has absorbed about 48% of the anthropogenic CO$_2$ (Sabine et al. 2004) thus acting as a sink and reducing the pace of global warming. The current ocean uptake is about 25% of the total of anthropogenic CO$_2$ emissions (Le Quéré et al. 2009).
As CO₂ dissolves at the ocean surface it reacts with water to form protons (H⁺) and inorganic carbon (DIC), which is the sum of the concentrations of carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻), and carbonate ions (CO₃²⁻) stored in the ocean. With increasing atmospheric pCO₂, DIC will increase and the equilibrium of the carbonate system will shift to higher CO₂ and bicarbonate ion-levels, lower carbonate ion concentration and lower pH (Wolf-Gladrow et al. 1999; Feely et al. 2009).

These changes in carbonate chemistry are already occurring, and often referred to as “ocean acidification” (OA), although pH will not shift below the neutral value of 7. Records of ocean carbon chemistry for the last 25 years show clear trends of increasing carbon and decreasing pH that follow increasing atmospheric CO₂, in agreement with estimates from basic marine chemistry (Bates 2007; Caldeira et al. 2007). The surface ocean has been acidified by 0.1 pH unit since 1800 (Orr et al. 2005). Current models predict that the pH of surface seawater will drop by an additional 0.2-0.4 pH units by the year 2100 (Caldeira & Wickett 2005; Sabine & Feely 2007; Feely et al. 2009).

Ocean warming and acidification are likely to have a large impact on marine life and biogeochemical processes, such as the dissolution of carbonate mineral and reduced production and accumulation of marine biogenic carbonates. Seawater acidification reduces the calcium carbonate (CaCO₃) saturation state (Kleypas et al. 2006), thus creating conditions less favourable to biogenic calcification (Raven et al. 2005; Atkinson & Cuet 2008; Hall-Spencer et al. 2008).

Saturation state has been shown to affect growth in calcifying green algae, crustose coralline algae, and corals (Gattuso et al. 1998; Seibel & Fabry 2003; Kleypas & Langdon 2006; Kleypas et al. 2006; Tyrrell 2008), which are among the key carbonate producers in coastal waters. Because the solubility of CaCO₃ increases at lower temperature and higher pressure, cold and deep ocean waters are naturally low in saturation or even undersaturated with respect to CaCO₃, becoming corrosive and dissolving carbonate minerals (Broecker 2003). Surface ocean waters at present are supersaturated with both aragonite and calcite, but the aragonite and calcite saturation horizons of the world’s oceans are shoaling at a rate of 1-2 m per year (Guinotte & Fabry 2008) due to the influx of anthropogenic CO₂ to the oceans. High-latitude surface waters like the southern Ocean will be undersaturated with respect to aragonite by 2050 (Orr et al. 2005), with calcite expected to follow 50-100 years later (Feely et al. 2004, 2008, 2009; Doney et al. 2009).

The anthropogenic increase of CO₂ has already shifted the saturation horizons for CaCO₃ towards the surface by 50-200 m above its position before the industrial revolution. So undersaturated deep waters is growing in extent upward and, by 2050, the saturated surface zone will begin to disappear in some areas (Feely et al. 2004, 2009).

The precipitation of calcium carbonate is a source of CO₂, whereas carbonate dissolution acts as a sink of CO₂ (Frankignoulle et al. 1994). Ultimately, carbonate dissolution is expected to buffer OA and play an important role in global change, but the natural process of carbonate dissolution is too slow to neutralize the fossil fuel CO₂ for it requires decades to centuries (Andersson et al. 2003). The lowered carbonate saturation state may cause a selective dissolution of metastable carbonate minerals in accordance with their relative solubilities. Current evidence suggests that a metastable equilibrium is maintained between the pore water and the most soluble carbonate mineral phase present in the sediments. Thus, dissolution could buffer the acidity of the pore waters in carbonate sediments, but overlying surface waters in coastal environments will not accumulate enough alkalinity to produce a significant buffer effect (Langdon 2000; Andersson et al. 2003, 2005; Andersson & Mackenzie 2011).

In addition to the process of calcification, respiration from aerobic biota is a major source of CO₂. On the other hand, photosynthesis removes CO₂ to produce new organic matter in plants, algae, and cyanobacteria. Therefore, calcifying photosynthetic organisms are at the same time sink and source of CO₂ but the algebraic result of these antithetic functions in calcareous-algae dominated environments is largely unexplored (Frankignoulle et al. 1994; Suzuki 1998).
BIOMINERALOGY AND MARINE ACIDIFICATION

Calcium carbonate occurs in invertebrate skeletons and algal thalli as aragonite or calcite. Magnesium (Mg$^{2+}$) can replace some of the Ca$^{2+}$ in the calcite lattice, and calcite containing > 4% wt of MgCO$_3$ is conventionally defined as high Mg-calcite (HMC; Tucker & Wright 1990; Ries et al. 2009), although the 4% boundary is arbitrary and not universally recognized (Rucker & Carver 1969; Smith et al. 2006; Andersson & Mackenzie 2011). The extent to which a biogenic carbonate particle is prone to dissolution in seawater depends on several factors, among which the leading ones are mineralogy and the calcium carbonate saturation state, which is dependent on the carbonate ion concentration (Mucci 1983; Gehlen et al. 2005).

Of the two major biologically secreted forms of CaCO$_3$ in modern calcifiers, aragonite has twice the solubility of pure calcite (Zeebe & Wolf-Gladrow 2001; Politi et al. 2004). However, natural biogenic HMC containing > 8-12 mol% MgCO$_3$ is more soluble than aragonite, so is the most sensitive responder to acidification (Morse et al. 2006; Andersson et al. 2008, 2011).

Shelf sedimentary facies of the temperate and cold zones are enriched in calcite and HMC, derived from bryozoans, foraminifers, coccolithophores, coralline algae and echinoderms, with red coralline algae as the most important contributor of HMC. In contrast, aragonite dominates the sediments of the tropical oceans, derived from scleractinian corals and green algae (a review of sedimentary facies is provided by Mutti & Hallock 2003).

Cool-water carbonate-rich sediments will be the first to suffer the impact of a decrease of the carbonate saturation of seawater (Morse et al. 2006; Andersson et al. 2008). Consequently, existing deposits of highly soluble HMC in the medium and high latitudes are likely to be the first to undergo dissolution caused by the ongoing OA. In order to assess the role of the medium and high-latitude HMC deposits on the total carbonate budget, and their possible buffer effect in a scenario of increasing acidification, their identification and quantification is strongly needed (Guinotte & Fabry 2008; Le Quéré et al. 2009). Field and laboratory experiments are needed to assess their rate of dissolution, because the observed solubility of biogenic carbonates shows a more or less pronounced offset from the theoretical behaviour described from synthetic, pure and compact minerals (Bischoff et al. 1983; Morse et al. 2006). Moreover, marine carbonate assemblages are multi-phase systems that are heterogeneous at the level of individual carbonate shell structure and composition, and at the level of particle characteristics (compactness, thickness, geometry, volume/surface ratio, etc.) (Walter & Morse 1984; Agegian & Mackenzie 1989). In this context, the focus will be on calcareous red algae.

THALLUS CALCIFICATION IN MODERN CALCAREOUS RHODOPHYTA

The largest group of present-day calcareous red algae (Rhodophyta) are corallines, of the orders Corallinales and Sporolithales (taxonomic reference in Guiry & Guiry 2011) (Figs 1; 2). The thallus of these calcified algae develops from a thin crust, composed of cell filaments that are connected together, and grows by division of the filaments and by addition of one new cell at the tip of each filament (Fig. 1A-C) (Johansen 1981; Cabioch 1988; Woelkerling 1988 for general reference to morphogenesis and anatomy).

The cell walls of the coralline thallus are composed of Mg-calcite, with [Mg] increasing in the calcite lattice as the temperature increases, in seawater with present-day Mg/Ca mole ratio (Chave 1954; Basso 1992; Halfar et al. 2000; Stanley et al. 2002; Basso
et al. 2006; Kamenos et al. 2008, 2009). The [Mg] of the thallus increases with increasing temperature and calcite saturation (Agegian 1985). Temperature is negatively correlated to calcite density of thin-walled cells, within annual or subannual banding patterns (Cabioch 1966; Adey & McKibbin 1970; Giraud & Cabioch 1979; Freiwald & Henrich 1994; Basso 1994, 1995; Halfar et al. 2000; Blake & Maggs 2003; Rivera et al. 2004; Basso et al. 2006; Kamenos & Law 2010). Growth rates increase with temperature, as evinced by a six-fold faster growth of *Lithophyllum margaritae* (Hariot) Heydrich incubated at 25°C than at 10°C (Steller et al. 2007b), although a large variability of response and adaptation

**Fig. 1.** — SEM photographs of the calcified thallus of coralline algae: **A**, calcified cell filaments in a protuberance of a non-geniculate plant. The empty conceptacle chambers on the border contained the non-calcified spores; **B**, a coralline growing margin showing the outermost non-calcified epithallial cell wall (white arrow). Below are the completely calcified perithallial cell walls with the primary (white arrowhead) and secondary (black arrow) Mg-calcite layers; **C**, chemical precipitation of carbonate druse inside an empty conceptacle chamber; **D**, a geniculate coralline alga with the articles (intergenicula) connected by flexible joints (genicula) made of uncalcified filaments (arrows); **E**, a close-up of a geniculum showing the non-calcified filaments (arrow). Scale bars: A, D, 250 µm; B, 10 µm; C, 100 µm; E, 50 µm.
is expected in other species from different climatic belts (Adey 1970). The growth rate of *Porolithon gardineri* (Foslie) Foslie dramatically decreased with temperature above 29-30°C, but it increased linearly as function of calcite saturation, and was only slightly influenced by light intensity (Agegian 1985). In agreement with Martin & Gattuso (2009) growth and calcification of coralline algae increase with increasing temperature, within the range in the natural habitat. Above these levels, warming is detrimental and causes necrosis and death.

After the release of spores, prismatic or acicular crystals of calcite or aragonite may form in the empty conceptacles or in other microcavities (Alexandersson 1974; Harney *et al.* 2000) (Fig. 1C). Moreover, brucite was detected in some corallines under XRD analysis (Moberly 1968), although this finding has been confirmed in recent literature.

Corallines are separated into two morpho-functional groups of no taxonomic value (Cabioch 1988): the geniculate (= articulate), with uncalcified flexible genicula alternating with rigid calcareous intergenicula, and the completely rigid non-geniculate, also referred to as crustose coralline algae or CCA (Figs 1; 2). Most genicula decompose after death, so geniculate corallines disarticulate into sand-sized particles and can accumulate in situ or be easily transported away from the original habitat. On the contrary, non-geniculate corallines inhabiting hard and soft substrates may enter the geologic record more or less in their original shape or produce fragments of any size: boulders derived from algal build-ups, rhodoliths several centimetres long, millimetric detached protuberances or crusts, and heavily abraded fine sand-sized fragments (Agegian & Mackenzie 1989; Tsuji 1993; Harney *et al.* 2000; Gherardi & Bosence 2001; Toscano & Sorgente 2002; Fornos & Ahr 2006; Hetzinger *et al.* 2006; Brandano & Civitelli 2007) (Fig. 2).

Geniculate and non-geniculate coralline algae are one of the most prolific carbonate producers among seagrass epiphytes worldwide (Land 1970; Nelsen & Ginsburg 1986; Walker & Woelkerling 1988; Perry & Beavington-Penney 2005). Together they are about 38-80% of the total of epiphyte-produced carbonate on seagrass leaves in southern Australia (James *et al.* 2009; Table 1). Encrusting epiphyte corallines are very thin and disintegrate rapidly when seagrass blades are broken or decomposed, becoming carbonate mud (Nelsen & Ginsburg 1986; Perry & Beavington-Penney 2005; James *et al.* 2009).

Other orders of red algae include calcified species, namely the aragonite precipitating Peyssonneliales and Nemaliales (taxonomic reference in Guiry & Guiry 2011; Chave 1984; Nelson 2009).

Peyssonneliales are a diverse group of platy, orbicular algae with a variable but species-specific degree of calcification (Fig. 3). Some Peyssonneliales possess only scattered calcified cells and a hypobasal, extracellular calcification, while a few species of *Peyssonnia* Decaisne such as *P. rosa-marina* Boudouresque & Denizot (Mediterranean, temperate) and some genera such as *Pohyrysta* Heydrich (warm temperate to tropical) are fully calcified (Fig. 3) (Denizot 1968; James *et al.* 1988; Basso 1990; Ballantine *et al.* 2000; Kato *et al.* 2006). The aragonite laid down within the cell wall is organized in layers of various thickness in which crystals are either spherulites or prisms oriented normal to the cell surface (Flajs 1977; James *et al.* 1988) (Fig. 3G). The hypobasal calcification appears as an aragonite crust 80-200 µm thick, projecting downward from the lower thallus surface and crossed by rhizoids (Fig. 3C, D).

The post-mortem fate of Peyssonneliales is largely dependent on their habit and growth-form (single crust on solid substrate; layered crusts, applanate or globose forming rhodoliths on soft substrate, foliose frameworks). However, as most of them do not form thick encrustations, they easily undergo fragmentation before final burial. Those Peyssonneliales possessing only the hypobasal calcification may also enter the sedimentary record as aragonite chip-like structures, which may be distinguished from simple layers of cement as long as the traces of rhizoids are preserved (James *et al.* 1988). Based on data from Ballesteros (1994), a western Mediterranean *Peyssonnia* bed, dominated by the completely calcified *P. rosa-marina*, contains 1477 to 2169 g m⁻² of algal carbonate, equivalent of a carbonate production of about 123-181 g m⁻² y⁻¹.

The calcareous species of Nemaliales occur in the genera *Galaxaura* Lamouroux, *Liagora* Lamouroux, *Izziella* Doty and *Titanophycus* Huismans, Saunders & Sherwood. The aragonite calcification and
the thallus are very variable, even within the same genus (Guiry & Guiry 2011; Lin et al. 2011). *Galaxaura* is found mainly in the tropics. *Liagora* is the largest genus in the family Liagoraceae and widely distributed in warm-water and temperate regions (Guiry & Guiry 2011; Lin et al. 2011).
The calcareous Nemaliales possess an articulated or inarticulated thallus, mostly erect, that after death is easily fragmented and transported.

The skeletal ultrastructure of *Galaxaura* was investigated by Okazaki *et al.* (1982) and Mu & Riding (1999), who found aragonite: 1) in the intercellular spaces of the algal cortex; 2) in the cell wall mostly in the form of granules; and 3) on the inner surface of the cortex as elongate crystals. The quantification of the carbonate production of Nemaliales has never been addressed, though it is not expected to be significant on global scale.

**RED CALCAREOUS ALGAE, GLOBAL CHANGE AND CARBONATE BUDGET OF NON-TROPICAL SHELVES**

The scientific literature started to re-evaluate the geologic role of coralline algae in the seventies (Adey & McIntyre 1973; Adey & Vassar 1975) and subsequently, the common occurrence of algal carbonates in non-tropical sediments started to be a shared knowledge among geologists. More recently, some comprehensive books, reviews and a number of scientific papers on non-tropical carbonates pointed out the importance of calcareous red algae as carbonate producer (among others: Nelson 1988; Canals & Ballesteros 1997; James & Clarke 1997; Foster 2001; Pedley & Carannante 2006).

Coralline algae are common from tropical to polar oceans at all depths within the photic zone and, contrary to the other groups of calcareous red algae (Peyssonneliales and Nemaliales), they are major framework builders and carbonate producers especially in temperate and cold water benthic ecosystems (Pérès 1982; Bosence 1983a; Nelson 1988; Freiwald & Henrich 1994; Fornos & Ahr 1997; James & Clarke 1997; Bressan *et al.* 2001; Foster 2001; Ballesteros 2006). The coralligenous habitat is an outstanding example of the role of carbonate bioconstruction (Bosence 1983a; Ballesteros 2006; Nalin *et al.* 2006; Basso *et al.* 2007).


The scientific literature on the relationship between coralline algae and the anticipated consequences of climate change, particularly global warming and OA, has been centred on three different levels: 1) the response of the individual organism; 2) the impact on the biological cycle of coralline species; and 3) the feedback to marine acidification from habitats dominated by coralline algae, i.e. their role as source or sink of atmospheric CO$_2$.

The investigations by field work and pH and T manipulation experiments have been aimed to test the following hypotheses (Kroeker *et al.* 2010; Table 1): 1) calcifying plants are more sensitive to ocean acidification than non calcified plants; 2) coralline algae are more sensitive than other organisms to OA because their HMC thallus is more soluble than pure calcite and can be the most soluble mineral phase when Mg > 8-12 mol% MgCO$_3$; and 3) some stages in their life history are more sensitive than other.
Response of calcifying vs non-calcifying algae

Photosynthesis by most macroalgae appears to be limited by inorganic carbon sources in natural seawater, although some results are contradictory (among others: Surif & Raven 1989; Mercado et al. 2001), and the ongoing rise in the atmospheric CO₂ is expected to have a positive effect in the growth of fleshy algae (Gao et al. 1993b; Hendriks et al. 2010; Kroeker et al. 2010).

Along a natural pH gradient from 8.1 to 6.7 caused by volcanic vents, macroalgal associations change at both taxonomic and morphological levels (Hall-Spencer et al. 2008; Porzio et al. 2011). The majority of the macroalgae grew with only a 5% decrease in species richness as the mean pH dropped from 8.1 to 7.8. However, at pH 7.8 the species richness declined 72%, and was associated with a marked decrease of cover by turf algae. Of the twenty species of calcareous algae occurring at normal pH, none was recovered at pH 6.7, and an overall reduced cover was observed at pH 7.8, with the exception of the non-geniculate coraline Hydrolithon cruciatum (Bressan) Chamberlain (Porzio et al. 2011). Unfavourable conditions for calcification in calcifying algae apparently give an advantage to the non-calcified algae that outcompete them for space and light (Porzio et al. 2011), although Langdon et al. (2003) saw an eight-fold decrease in the calcification of a coral reef com-

![Image](image-url)

Fig. 3. — The calcified thallus of Peyssonellales: A, Peyssonella rosa-marina Boudouresque & Denizot rhodolith from the Mediterranean sea; B, Peyssonella sp. crustose growth-form from Mediterranean hard substrates; C, the calcified thallus of the aragonitic Peyssonella Decaisne and the hypobasal calcification (arrow); D, a non calcified Peyssonella with rhyzoid traces across the hypobasal calcification (arrow); E, a thick rhodolith-forming Polysrrata Heydric; F, detail of Polysrrata thall; G, close-up of calcified cell-walls of Polysrrata. Note spherulitic crystals; C-G, SEM photographs. Scale bars: A, B, 2 cm; C, 50 μm; D, 40 μm; E, 250 μm; F, 20 μm; G, 2 μm.
Community dominated by macroalgae in response to a doubled pCO$_2$, accompanied by enhanced turnover of organic carbon and absence of effect on net organic production.

Mesocosm experiments exposing CCA to elevated pCO$_2$ (2 × present day) indicate up to a 92% reduction in total area covered by CCA and a 52% increase in soft-bodied algae (Guinotte & Fabry 2008; Kuffner et al. 2008). 

**Coralline algae calcification in response to OA and risen temperature**

A long-term experiment in a coral reef mesocosm showed that a pCO$_2$ double than present results in an 86% decrease of the total coralline cover on hard surfaces, and 250% decrease in the calcification of rhodoliths (Jokiel et al. 2008). Combined field work observations along natural gradient of acidification (volcanic venting) and pH manipulation in aquaria show that coralline epiphytes on *Posidonia* leaves decrease from 18-69% cover in normal seawater to nil at pH 7.7, with complete dissolution at pH 7 (Martin et al. 2008). However, an investigation of the response of *Neogoniolithon* Setchell & Mason to pCO$_2$ values of modern concentration, 2, 3 and 10 times the pre-industrial levels, gave a complex response: net calcification appears to increase from pre-industrial to present-day [CO$_2$], remains more or less stable with doubled [CO$_2$], and decreases under the highest pCO$_2$ (Ries et al. 2009).

Under experimental conditions of elevated temperature (ambient + 3°C) and elevated pCO$_2$ (700 ppm), the percentage of CCA deaths doubled or tripled, and was accompanied by a rate of dissolution of dead algal thalli two to four times higher (Martin & Gattuso 2009). Net calcification is reduced by half under elevated temperature and pCO$_2$ (Martin & Gattuso 2009). High CO$_2$ and warming at 28-29°C are bleaching agents for CCA under high irradiance (Anthony et al. 2008), with calcification reduced by 50% at pH 7.8 and net dissolution occurring at pH 7.6 (Anthony et al. 2008).

**Sensitivity to OA and risen temperature during life cycle**

The recruitment rate and growth of coralline algae is severely inhibited under elevated pCO$_2$, although the reduced coralline cover along a natural gradient of increased CO$_2$ is associated with relative increase of the reproductive structures at pH 7.8 in the non geniculate genera *Neogoniolithon* and *Mesophyllum* Lemoine, and a decrease in the geniculate *Jania* Lamouroux (Porzio et al. 2011). Agegian (1985) also reported a reduction in recruitment when CCA are exposed to elevated pCO$_2$ in aquarium experiments (Guinotte & Fabry 2008). Mesocosm experiments exposing CCA to pCO$_2$ double than present indicate up to a 40% reduction in growth rates and 78% decrease in recruitment (Buddemeier 2007; Kuffner et al. 2008).

A study on the effect of marine acidification on Corallinales spores in an artificial controlled culture showed inhibition of coralline spore production and growth, and increase in the mortality of germination disks (Cumani et al. 2010).

**Quantification of coralline carbonates**

During the last decades, ongoing global change became one of the biggest scientific challenges of our time, demanding an improved knowledge and quantification of the C pathways between lithosphere, hydrosphere, atmosphere, and biosphere, and of the response of each component of the system to variations in physical and chemical parameters. One piece in the puzzle is the calcifying marine biota, and an increasing number of investigations appeared, aimed at understanding the sensitivity of organisms and biomes to global change (among others: Gao et al. 1993a, b; Gattuso et al. 1996, 1999; Riebesell et al. 2000; Orr et al. 2005; CIESM 2008; Doney et al. 2009; Ries et al. 2009; Gao & Zheng 2010). Modelling the response of the oceans to increasing [CO$_2$] requires also a quantification of the total carbonate and its mineralogy on a global scale (Milliman 1995; Kleypas et al. 2006; Morse et al. 2006; Andersson et al. 2008).

Under favourable oceanographic conditions, the carbonate mass produced by coralline algae is dependent on their morphology (e.g., geniculate or non-geniculate, thick excrescent crusts or thin superposed foliose thalli; Woelkerling et al. 1993) and...
Table 1. — Literature compilation of results from manipulation of corallines by simulating OA and rising temperature. Abbreviations: \textit{decr.}, decrease; \textit{inc.}, increase.

<table>
<thead>
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<tr>
<td>Agejan 1985 reported by Kleypas et al. 2006</td>
<td>Porolithon gardineri (non geniculate), Hawaii</td>
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<td>Gao et al. 1993a</td>
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<td>Halimeda cubense and Amphiroa fragilisima (geniculate corallines), Chondria dasyphylla, Gelidiopsis intricata</td>
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<td>doubled carbon turnover; calcification: 85% decr.; no net increase in net primary production</td>
</tr>
<tr>
<td>Hall-Spencer et al. 2008</td>
<td>Amphiroa rigida, Corallina spp., Jania spp., Mesophyllum lichenoides, Lithophyllum incrustans</td>
<td>naturally acidified seawater, Mediterranean</td>
<td>Shift from dominant corallines to fleshy algae with pH 7.8; corallines absent at pH 7.2 or lower; no coralline epiphytes on Posidonia leaves at pH 7.6</td>
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<td>Anthony et al. 2008</td>
<td>Porolithon onkodes</td>
<td>acified mesocosm [CO$_2$] = present $\times 2$ and $\times 3$; temp. = 25-26°C; high natural irradiance</td>
<td>bleaching: 10% and 20% inc.; productivity: 50% and 100% decrease; calcification: 0% and 130% decrease (2$\times$ and 3$\times$ [CO$_2$] respectively)</td>
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<tr>
<td>Anthony et al. 2008</td>
<td>Porolithon onkodes</td>
<td>acified mesocosm [CO$_2$] = present $\times 2$ and $\times 3$; temp. = 28-29°C; high natural irradiance</td>
<td>bleaching: 10% and 30% inc.; productivity: negative values; calcification: 50% and 190% decrease (2$\times$ and 3$\times$ [CO$_2$] respectively)</td>
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<td>continuous flow acified coral reef mesocosm, Hawaii, [CO$_2$] = present $\times 2$</td>
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<tr>
<td>Martin &amp; Gattuso 2009</td>
<td>Lithophyllum cabiocheae</td>
<td>acified and warmed aquaria, Mediterranean [CO$_2$] = 700 ppm; T = ambient $\pm$ 3°C</td>
<td>calcification: 50% decrease; death from elevated T, increasing with [CO$_2$]</td>
</tr>
<tr>
<td>Ries et al. 2009</td>
<td>Neogoniolithon sp.</td>
<td>acified aquaria at 25°C and [CO$_2$] = 409; 606; 903; 2856 ppm</td>
<td>net calcification increase up to [CO$_2$] = 606 ppm; decreasing with higher concentrations inhibition of spore production and growth; increase of mortality</td>
</tr>
<tr>
<td>Cumani et al. 2010</td>
<td>Lithophyllum incrustans</td>
<td>acified mesocosm [CO$_2$] = 550 and 760 ppm</td>
<td>inhibition of spore production and growth; increase of mortality</td>
</tr>
<tr>
<td>Porzio et al. 2011</td>
<td>encrusting and geniculate CCA in a macroalgal community</td>
<td>naturally acidified seawater, Mediterranean</td>
<td>coralline species richness: 25% decrease and change of dominant species at pH 7.8; absent at pH 6.7</td>
</tr>
</tbody>
</table>
growth rate. Literature on growth-rate of coralline algae has been reviewed recently by Foster (2001).

On a global scale, few studies have focused on the quantitative contribution of biogenic carbonate and particularly on carbonate production and accumulation by coralline algae. A compilation of existing data shows that carbonate production by coralline algae spans four orders of magnitude, with the highest rates in tropical reefs, in the Mediterranean infralittoral community dominated by the geniculate *Corallina elongata* Ellis & Solander and in the maerl beds of the French Atlantic. The lowest values of carbonate production are from temperate seagrass epiphyte and deep soft-bottom assemblages (Table 2). Interestingly, this three first order carbonate producers among corallines are all shallow-water dwellers and include geniculate and non-geniculate, hard-substrate and free-living growth forms in a wide latitudinal belt.

Modelling the response of the benthic system of entire basins to environmental perturbations requires the identification of more or less homogeneous sea-floor areas and knowledge of their specific contribution to the carbonate budget in terms of carbonate production and sedimentation rate, mineralogy, and susceptibility to dissolution (Milliman 1993). Literature data on carbonate component distribution over large areas frequently has no sufficient detail to allow biogeochemical quantification. Furthermore, contributions dealing with sediment geochemistry either do not consider the biogenic components or are very detailed but their scale is too small for calculation of budgets.

Direct habitat mapping and sampling by SCUBA diving is currently considered the method most adequate and appropriate for shallow-water habitat characterization and the quantification of benthic components (among others: Coggan et al. 2007; Steller et al. 2007a; Peña & Barbara 2009). Deep-water benthic habitats can be mapped at the meso-scale by bathymetric data and seismic profiles integrated with point-based information (sea-bed samples) for “ground-truthing” of the substrate and biota (Kenny et al. 2003; Coggan et al. 2007; Savini et al. 2012).

These methods not only allow qualitative identification and mapping of benthic habitats, but also quantification of the carbonate contribution of biogenic components and specific mineral phases over large areas, provided that sediment analysis of representative samples is coupled with X-Ray diffractometry (Bracchi & Basso 2012).

**DISCUSSION AND CONCLUSIONS**

Although some recent investigations and meta-analysis of available literature pointed out the variable effects of OA on marine biota (e.g., Ries et al. 2009; Hendriks et al. 2010; Kroeker et al. 2010), a considerable body of evidence indicates that crustose coralline algae are one of the most vulnerable benthic element to the negative biological and chemical effects of OA and global warming (Table 1).

Since by the end of this century net dissolution is likely to exceed net calcification in coralline algae, we expect dramatic consequences in terms of changes in biodiversity and biogeochemistry, especially in those habitats dominated or literally built by these algae, outside the tropical belt (Ballesteros 2006; Martin & Gattuso 2009).

The susceptibility of coralline algae calcification to marine acidification has been confirmed and related to the solubility of their Mg-calcite thalli (Kuffner et al. 2007; Hall-Spencer et al. 2008; Martin & Gattuso 2009). So an important question requiring further investigation is assessment of the solubility of natural coralline-rich build-ups and sediments, that will vary considerably as function of the mean Mg content of their thalli.

Available estimates of the total biogenic carbonate volume in the world oceans are affected by large uncertainties, mainly due to the lack of trustworthy data on carbonate mass accumulation rates (Milliman 1993). On a world basis the coastal benthic habitats already characterized and mapped at sufficient detail are far from representative of the whole (Hetzinger et al. 2006; Nelson 2009).

Even in the relatively well-studied Mediterranean Sea the distribution of important benthic facies, such as those dominated by corallines on both hard and soft bottoms, is largely unknown (Ambelas et al. 2004), thus introducing a bias in predicting the response of the shelves to global change. About 5% of the Mediterranean Sea is shallower
than 100 m. Given the lack of reliable data on the distribution of highly productive (coralline) habitats, in a conservative hypothesis of 5 g m\(^{-2}\) y\(^{-1}\) produced on average by coralline algae across the shelf < 100 m, we obtain a Mediterranean coralline carbonate production of \(0.65 \times 10^6\) t y\(^{-1}\), with large local variation (Table 2).

Locating and describing the algal carbonate factories, and the evaluation of their extent and production are a priority for future research, as a tool for...
the environmental management of these hot-spots of biodiversity and to obtain a reliable carbonate budget for the world shelves.

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